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Kinetics of $CaCO_3$ Scale in Waters Stabilized by CO_2

2

Calcium Carbonate Scale Dissolution in Water Stabilized by Carbon Dioxide Treatment

by
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Calcium carbonate scale in potable water systems (especially hot-water pipes and exchangers) can restrict pipe flow, causing severe head loss and reducing heat transfer capacity. Chemical and mechanical methods of cleaning the distribution systems are considered unsafe for potable supplies due to the human health hazard. As a result, the only alternative may be complete pipe replacement--which can be very expensive.

The U.S. Army Construction Engineering Research Laboratory (USACERL) and Illinois State Water Survey have jointly developed a carbon dioxide treatment system for rehabilitating clogged pipes and controlling scale buildup in nonfouled systems. The treatment method is safe and effective. It is being field-tested successfully at several Army installations.

Information is needed on the characteristics of scale dissolution for optimizing the treatment system because overdoses of carbon dioxide can eventually damage pipes. Therefore, USACERL has explored several models for predicting the effects of carbon dioxide treatment on potable waters. A theoretical model was formulated and used in developing a computer program for assessing a water's propensity to become undersaturated, saturated, or oversaturated with respect to carbon dioxide, and to determine its capacity for calcium deposition or dissolution.

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FOREWORD

This work was performed by the U.S. Army Construction Engineering Research Laboratory (USACERL) under Project 4A161102AT23, "Basic Research in Military Construction"; Work Unit CO-015, "Kinetics of $CaCO_3$ Scale in Waters Stabilized by CO_2."

The research was conducted by the USACERL Environmental Division (EN). Dr. R.K. Jain is Chief, EN. John Harwood is with Tennessee Technological University.

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COL Carl O. Magnell is Commander and Director of USACERL, and Dr. L.R. Shaffer is Technical Director.

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CALCIUM CARBONATE SCALE DISSOLUTION IN WATER STABILIZED BY CARBON DIOXIDE TREATMENT

1 INTRODUCTION

Background

Natural waters from carbonaceous aquifers are generally saturated with calcite, which tends to deposit calcium carbonate scale in water distribution pipes if the water is not stabilized. Current water treatment practices recommend production of slightly scaling water so as to form a layer of calcium carbonate scale in pipes to prevent corrosion. However, if left unchecked, the calcium carbonate scale will eventually accumulate in the pipes, especially in hot-water heat exchangers and hot-water circulation systems in buildings. Many Army installations both inside and outside the continental United States have scaling problems in their distribution systems.

Water-formed scale deposits in plumbing systems can restrict pipe flow, causing severe head loss and reducing heat transfer capacity in water heating systems. Further, when pipes become clogged with scale deposits, they may need to be replaced, incurring large capital costs. An alternative to replacement is rehabilitation, which can avoid the replacement costs, reduce energy consumption, and extend the lifespan of the plumbing system. However, current methods for removing scale (acid cleaning, various chemical treatments, and mechanical cleaning) are not suitable for domestic water supplies because of the associated health hazards.

An innovative technique of using carbon dioxide to selectively dissolve calcium carbonate scale in potable water systems has been developed by the U.S. Army Construction Engineering Research Laboratory (USACERL) in conjunction with the Illinois State Water Survey. Details of this technique are described in a USACERL Technical Report.[1] This approach is being field-tested at several Army installations; preliminary results are very promising. The advantages of carbon dioxide treatment are that it is safe and effective, and can be applied without a system shutdown. A potential drawback, however, is that too high a dose can be corrosive to pipes. Therefore, further research is needed to understand the fundamental process of scale dissolution. A method of predicting the scale deposition/ dissolution properties of different waters would be useful in designing the optimal carbon dioxide treatment system.

Objective

The objective of this study was to develop a method to predict the calcium carbonate dissolution characteristics of waters stabilized by carbon dioxide treatment.

Approach

A literature review identified several theoretical models for characterizing calcium carbonate dissolution. These models were evaluated to determine their potential in predicting whether a water is

[1]T. Prakash, C. Neff, R. Scholze, J. Bandy, and E. Smith, *Carbon Dioxide Treatment for Scale Removal and Control in Potable Water Systems,* Technical Report N-87/16/ADA184346 (U.S. Army Construction Engineering Research Laboratory [USACERL], May 1987).

undersaturated, saturated, or oversaturated with respect to calcium carbonate and the water's capacity for calcium carbonate deposition or dissolution. Based on the findings, a theoretical model was developed and used to create a computer program in BASIC language to predict the effects of carbon dioxide treatment on potable waters.

Scope

This report describes the development of a theoretical model to predict the effects of carbon dioxide treatment on calcium carbonate scale dissolution in potable waters. Research and development on the carbon dioxide treatment system were described in Technical Report N-87/16. Results of field-testing the treatment system at Army installations will be published in a future Technical Report.

Mode of Technology Transfer

The results of this research will be applied directly to the ongoing 6.2 project "In-Service Rehabilitation of Scaled Water Systems." In addition, the U.S. Army Engineering and Housing Support Center (USAEHSC) is expected to incorporate the model as a part of the Operator Assistance Program. among the potential users are installation Directorates of Engineering and Housing (DEHs), whose responsible utilities include overseeing the hot-water distribution and plumbing systems.

2 CALCIUM CARBONATE DISSOLUTION CHARACTERISTICS IN WATER

There are two major aspects to consider in modeling the effects of carbon dioxide treatment on water in removing or preventing calcium carbonate scale. The first aspect deals with the equilibrium of calcium carbonate in water. Equilibrium reactions are generally based on the water characteristics such as pH, alkalinity, and calcium concentration, and are represented in terms of saturation indexes. These indexes define the water's ability to deposit or dissolve calcium carbonate. The second aspect of this study involves the solution kinetics of calcium carbonate. In other words, an attempt must be made to define the rate at which calcium carbonate is dissolved or deposited from a specific water under specific environmental conditions. Very few studies in the literature deal with calcium carbonate dissolution kinetics. Those available mainly describe natural dissolution of calcium carbonate in underground environments and seawaters.

Calcium Carbonate Saturation Indexes

Chemical models of calcium carbonate equilibrium reactions are expressed in terms of a calcium carbonate saturation index. Several indexes of calcium carbonate saturation have been developed, including the Langelier, Ryznar, Aggressiveness, Driving Force, Momentary Excess, and Calcium Carbonate Precipitation Potential indexes. Methods for computing these saturation indexes and an evaluation of their performance are summarized below.[2] Table 1 presents the ranges and relative significance for each index.

Table 1

Saturation Indexes Ranges and Relative Significance

Index	Undersaturated Systems	Saturated Systems	Oversaturated Systems
Langelier Index (LI)	negative LI	LI = zero	positive LI
Ryznar Index (RI)	RI > 7	RI ≈ 7	RI < 7
Driving Force Index (DFI)	DFI < 1	DF = 1	DFI > 1
Aggressiveness Index (AI)	AI < 10 highly aggressive	10 ≤ AI ≥ 12 moderately aggressive	AI > 12 nonaggressive (i.e., protective)
Momentary Excess (ME)	negative ME	ME = zero	positive ME

[2] J.R. Rossum and D. T. Merrill, "An Evaluation of the Calcium Carbonate Saturation Indexes," *Journal of the American Water Works Association (JAWWA)* (February 1983).

The saturation index computation is based on the following fundamental equations:

$$(H^+)(OH^-) = K_w' \qquad \text{[Eq 1]}$$

$$(H^+)(HCO_3^-)/(H_2CO_3) = K_1' \qquad \text{[Eq 2]}$$

$$(H^+)(CO_3^{2-})/(HCO_3^-) = K_2' \qquad \text{[Eq 3]}$$

$$(Ca^{2+})(CO_3^{2-}) = K_s' \qquad \text{[Eq 4]}$$

$$(Mg^{2+})(OH^-) = K_m' \qquad \text{[Eq 5]}$$

$$Alky = (HCO_3^-) + 2(CO_3^{2-}) + (OH) - (H^+) \qquad \text{[Eq 6]}$$

$$Acy = (HCO_3^-) + 2(H_2CO_3) + (H^+) - (OH^-) \qquad \text{[Eq 7]}$$

The value for pHs, which is the pH of the system if saturated with calcium carbonate at the measured calcium and alkalinity values, is determined as follows:

$$Acy = P \cdot Alky + P \cdot Q + Q \qquad \text{[Eq 8]}$$

$$2K_s' RP/(Acy - Q) - (Acy - Q)/P + Q - 2\,(Ca^{2+}) + Alky = 0 \qquad \text{[Eq 9]}$$

where:

$$P = (1 + 2(H^+)/K_1')/(1 + 2K_2'/(H^+))$$

$$Q = (H^+) - K_w'/(H^+)$$

$$R = 2 + (H^+)/K_2'$$

$$(H^+)_s = (-B + \sqrt{B^2 - 4AC})2A \qquad \text{[Eq 10]}$$

where:

$$A = 1 - K_2'\,(Ca^{2+})Alky/K_s'$$

$$B = K_2'(2 - (Ca^{2+})Alky/K_s'$$

$$C = K_2'\,K_w'\,(Ca^{2+})/K_s'$$

Langelier Index

The first and by far the most commonly referenced index is the Langelier Saturation Index.[3] This index is defined as:

$$LI = pH - pHs \qquad \text{[Eq 11]}$$

where pH is the measured pH of the water and pHs is the pH of the system saturated with calcium carbonate at the measured value of calcium and alkalinity values (Eq 10).

Snoeyink and Jenkins[4] have modified the definition of pHs as the pH of the system if saturated with calcium carbonate at the measured calcium and bicarbonate values. The following equation is used to calculate pHsn:

$$[H^+]sn = [Ca^{2+}] \left(Alk - \frac{K'_n}{[H^+]} + [H^+] \right) x \left(\frac{K'_2}{K'_s} \right) \left(\frac{[H^+]}{2K'_2 + [H^+]} \right)$$

$$pHsn = -Log\,[H^+]sn \qquad \text{[Eq 12]}$$

The Langelier Index calculation using pHsn is represented by:

$$LIsn = pH - pHsn \qquad \text{[Eq 13]}$$

Ryznar Index

Another commonly used index is the Ryznar Index,[5] which is defined as:

$$RI = 2\ pHs - pH \qquad \text{[Eq 14]}$$

Ryznar conducted experiments showing that calcium carbonate was deposited on glass tubing at values of RI less than about 7.

Driving Force Index

The Driving Force Index (DFI) is defined by the following equat

$$DFI = \frac{[Ca^{2+}]\ [CO^{2-}]}{K's} \qquad \text{[Eq 15]}$$

[3]W. F. Langelier, "The Analytical Control of Anti-Corrosion Water Treatment," *JAWWA*, Vol 28, No. 10 (October 1936).
[4]V. Snoeyink and D. Jenkins, *Water Chemistry* (John Wiley and Sons, New York, 1980).
[5]J. W. Ryznar, "A New Index for Determining Amount of Calcium Carbonate Scale Formed by Water," *JAWWA*, Vol 36, No. 4 (April 1944).

Aggressiveness Index

The Aggressiveness Index (AI) was developed primarily for asbestos-cement pipe and is defined as:

$$AI = pH + \log_{10} \{Ca^{2}\} + \log_{10} \{Alk\} \qquad \text{[Eq 16]}$$

where:

$\{Ca^{2+}\}$ and $\{Alk\}$ are concentrations in mg $CaCO_3$/L.

The AI defines a water's corrosivity toward asbestos-cement pipe for waters in the range of 4 to 27 °C. Waters with an AI less than 10 are considered to be highly aggressive; those with an AI between 10 and 12 are moderately aggressive; and those with an AI exceeding 12 are considered nonaggressive or protective.

Momentary Excess

The Momentary Excess (ME) index defined by Dye[6] is calculated by solving the following quadratic equation:

$$ME = \frac{-B - B^{2} - 4AC}{2A} \qquad \text{[Eq 17]}$$

where:

$$A = 1$$

$$B = -[Ca^{2+}] - Alk + [H^{+}] - \frac{K'_w}{[H^{+}]} \quad \frac{K'_w}{[H^{+}] = 2K'_2}$$

and:

$$C = K'_s + [Ca^{2+}]\ Alk + [H^{+}] - \frac{K'_w}{[H^{+}]} \quad \frac{K'_2}{[H^{+}] + 2K'}$$

A positive ME denotes an oversaturated water, a negative ME denotes an undersaturated water, and an ME of zero denotes a saturated water.

[6] J. F. Dye, "Calculations of the Effect of Temperature on pH, Free Carb[illegible] and the Three Forms of Alkalinity," *JAWWA*, Vol 44, No. 4 (April 1952).

Calcium Carbonate Precipitation Potential (CCPP)

Merrill and Sanks[7] defined the CCPP to denote the quantity of calcium carbonate that can theoretically be precipitated from oversaturated waters or dissolved by undersaturated waters. The analytical solution for CCPP is described by Rossum and Merrill, and a computer program for calculating CCPP is provided in Appendix A.

Comparison of Saturation Indexes

Using CCPP as a benchmark, the above indexes were compared. The relationship between the indexes as a function of pH for a water c ntaining 50 mg calcium/L and 50 mg alkalinity/L is shown in Figure 1. The figure shows that no index correlates well with CCPP. The LI, RI, and AI are straight lines over the entire range of pH values and clearly bear no relationship to CCPP. The DFI, ME, and LIn display the hump-backed curve characteristic of CCPP to the right of pHs1. To the left of pHs1, however, they do not simulate CCPP at all. Hence, these indexes do not simulate a water's capacity to deposit or dissolve calcium carbonate in the same way as CCPP.

The CCPP index is better suited to describe calcium carbonate precipitation and dissolution.[8] CCPP accurately portrays whether a water is oversaturated, saturated, or undersaturated over the entire range of pH values. By definition, CCPP is the water's capacity to deposit or dissolve calcium carbonate and is directly related to the rate at which these processes occur.

Solution Kinetics of Calcium Carbonate

Relatively few investigations have addressed the effects of carbon dioxide dependence on the rate of calcium carbonate dissolution. Most of these studies have used naturally occurring calcite crystals and proposed kinetic models of dissolution based on experiments.

The rate of calcium carbonate dissolution is known to depend on the hydrodynamic conditions of the environment and on the rate of heterogeneous reaction at the surface. Numerous laboratory studies have demonstrated transport and surface-controlled aspects of calcium carbonate reactions in aqueous solutions.[9] The chemical species involved in the dissolution of calcite in carbonic acid are:[10]

$$CO_2(g),\ H_2O,\ CO_2(aq),\ H_2CO_3,\ H^+,\ HCO_3,\ CaCO_3(s),$$

$$Ca^{2+},\ CO_3^{2-},\ CaHCO^+_3,\ \text{and}\ CaCO_3$$

[7] D. T. Merrill and R. L. Sanks, "Corrosion Control by Deposition of Calcium Carbonate Films: A Practical Approach for Plant Operators," *JAWWA*, Vol 69, No. 11 (November 1977).

[8] D.T. Merrill and R.L. Sanks.

[9] L. N. Plummer and D. L. Parkhurst, "The Kinetics of Calcite Dissolution in CO_2-Water Systems at 5° to 60°C and 0.0 to 1.0 atm CO2," *American Journal of Science*, Vol 278 (1978); R. L. Curl, "Critical Review of the Kinetics of Calcite Dissolution and Precipitation" *Chemical Modeling in Aqueous Systems* (E.A. Jenne, Ed.), ACS Symposium Series 93 (American Chemical Society, 1979); R. A. Berner and J. W. Morse "Dissolution Kinetics of Calcium Carbonate in Sea Water," Part IV. Theory of Calcite Dissolution," *American Journal of Science*, Vol 274 (February 1974); P. K. Weyl, "The Solution Kinetics of Calcite," *Journal of Geology*, Vol 66, (1958); L. N. Plummer and R. D. Mackenzie, *Geochim. Cosmochim. Acta.*, Vol 40, (1976).

[10] R. L. Curl (1968).

The first five are supplied to the bulk of the solution and diffuse to the surface, where reaction with $CaCO_3(s)$ occurs. The rest are produced primarily at the surface and diffuse back into the solution.

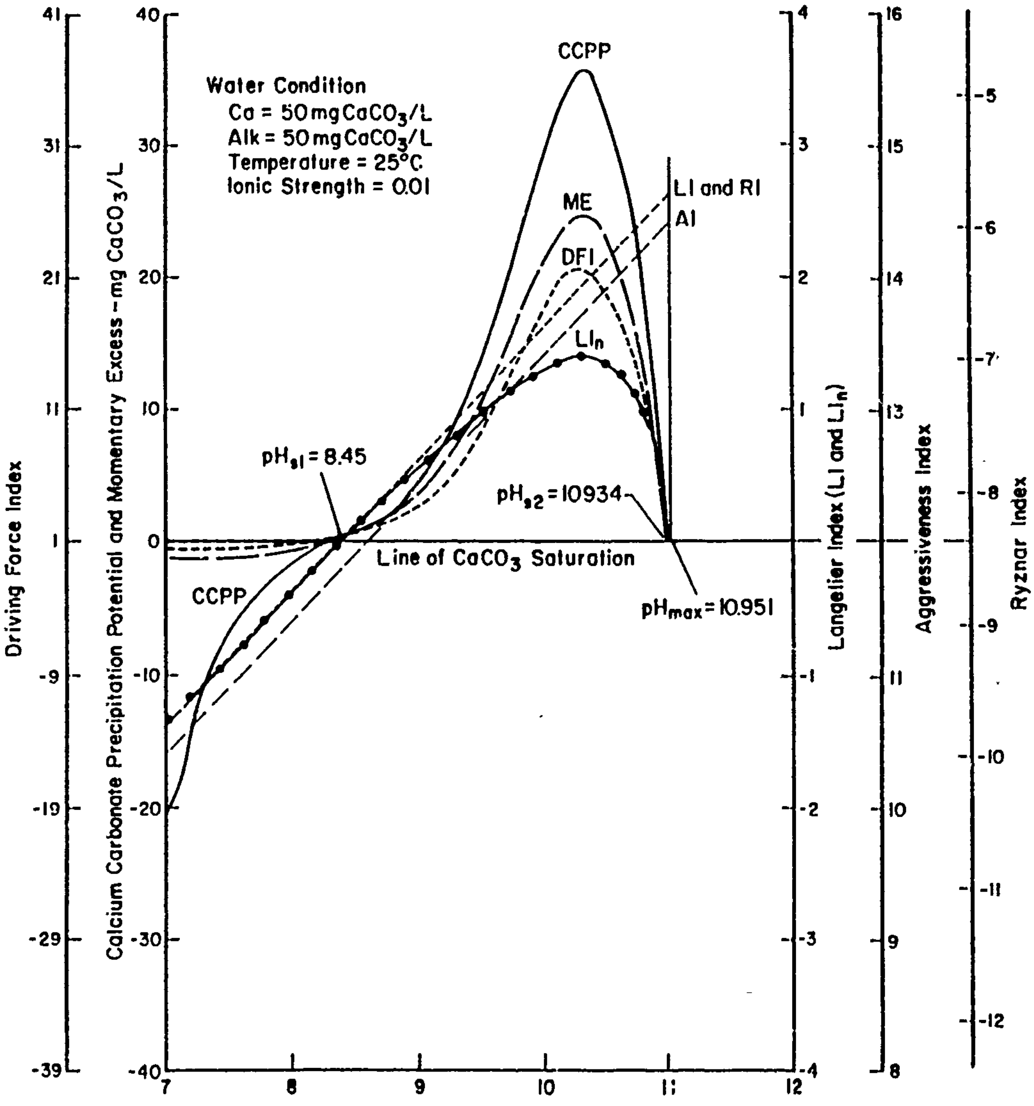

Figure 1. Saturation indexes vs. pH.

Weyl[11] proposed a model of limestone dissolution in sedimentary rocks. The solution kinetics were shown to depend on the rate at which water entering the rock becomes saturated, which, in turn, is governed by the transport of solute away from the solid-liquid interface.

The solubility of calcite in water for temperatures between 100 and 300 °C, at partial pressures of carbon dioxide ranging from 1 to 40 atmospheres, was reported by Ellis.[12] From a study of the kinetics of solution for a single calcite crystal, the rate-determining step was found to be a diffusion or desorption process.

Berner and Morse[13] presented a theoretical explanation, in terms of controlling reaction mechanisms, for the complex relationship between the rate of dissolution and undersaturation. Dissolution rate was found to be less than that predicted for control by ionic diffusion at pH values greater than 4.

Plummer et al.[14] reported results of experimental dissolution studies in a pure calcite-water system using the "pH-stat" and "free drift"[15] methods. The "pH-stat" method identified three forward rate dependencies far from equilibrium:

1. First-order dependence on the bulk fluid activity of H^+.

2. Linear dependence on the bulk fluid P_{CO_2}.

3. A constant forward rate in the near absence of H^+ and dissolved CO_2. The "free drift" method was used to study the rate of dissolution as the reaction approaches equilibrium. A mechanistic model based on the experimental results was proposed. The (net) rate of dissolution (R) is given by the equation:

$$R = k_1 a_{H^+} + k_2 a_{H_2CO_3} + k_3 A_{H_2O} - k_4 A_{Ca^{2+}} + A_{HCO_3^-}$$

where k_1, k_2, and k_3 are first-order rate constants dependent on temperature, and k_4 is a function of both temperature and P_{CO_2}. Estimates for the four rate parameters were calculated. The dominant reaction mechanisms in dissolution kinetics are shown in Figure 2.

Summary of Models Found in Literature

The chemical models presented in the literature to describe calcium carbonate equilibrium conditions for a water do so in terms of a water's capacity to dissolve or precipitate $CaCo_3$. The LI_{sn}, DFI, and ME are satisfactory indicators of whether a water is oversaturated, saturated, or undersaturated with respect to $CaCO_3$. However, they cannot predict the capacity of a specific water to dissolve or deposit $CaCO_3$. The LI, RI, and AI are unsatisfactory indicators of water's saturation state. CCPP is the index (by definition) best suited to determine the water's capacity to deposit or dissolve $CaCO_3$ and is directly related to the rate at which these processes occur.

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[11]P. K. Weyl.
[12]A. J. Ellis, "The Solubility of Calcite in Carbon Dioxide Solutions," *American Journal of Science*, Vol 257 (May 1959).
[13]R. A. Berner and J. W. Morse.
[14]L. N. Plummer; T. M. L. Wigley, and D. L. Parkhurst.
[15]R. A. Berner and J. W. Morse.

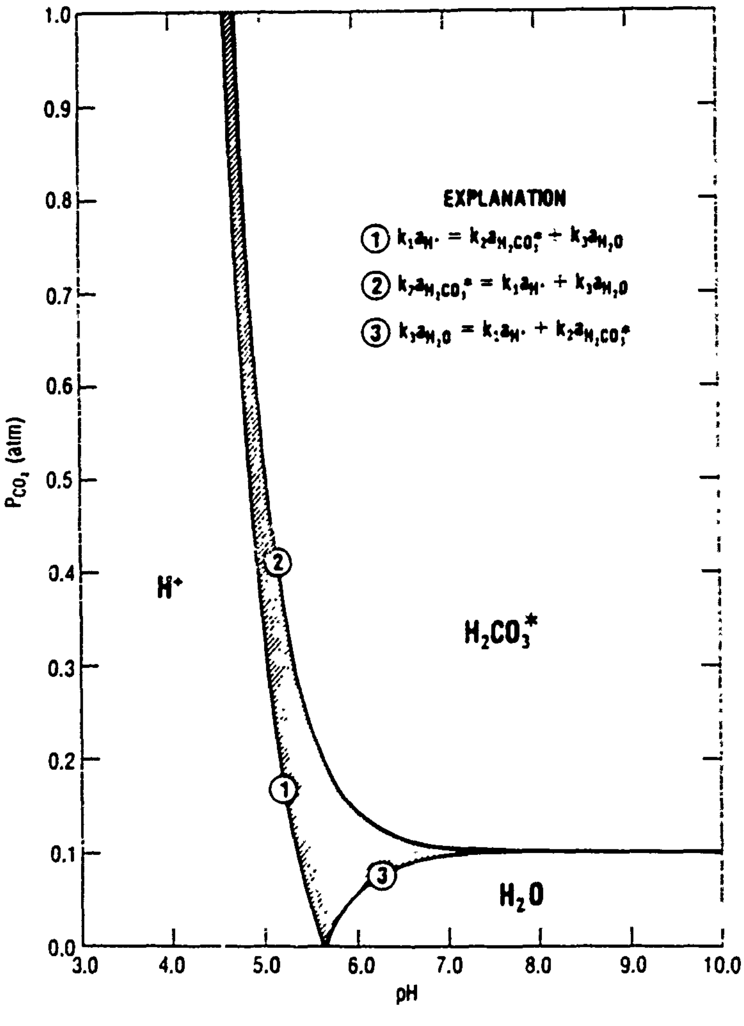

Figure 2. **Reaction mechanism contributions to the forward rate of reaction as a function of pH and P_{CO_2} at 25 °C.** Although H^+, $H_2CO_3^*$, and water reaction with calcite occur simultaneously throughout (far from equilibrium, as well as at equilibrium), the forward reaction is dominated by reaction with single species in the fields shown. More than one species contributes significantly to the forward rate in the shaded area, and along the lines labeled 1, 2, and 3, the forward rate attributable to one species balances that of the other two (1). (Source: Plummer, L. N., T.M. L. Wigley, and D. L. Parkhurst, "The Kinetics of Calcite Dissolution in CO_2-Water Systems at 5° to 60° and 0.0 to 1.0 atm CO_2," *American Journal of Science, Vol 278 [1978].* Curl, R., "Critical Review of the Kinetics of Calcite Dissolution and Precipitation," *Chemical Modeling in Aqueous Systems* [E.A. Jenne, Ed.], ACS Symposium Series 93 [American Chemical Society, 1979].

3 A COMPUTER MODEL TO DETERMINE THE EFFECT OF CARBON DIOXIDE TREATMENT ON POTABLE WATERS FOR SCALE REMOVAL

USACERL developed a theoretical model based on the published models that appeared to be most appropriate to this research. Using the theoretical model, a computer program called "CO_2 TRT PLOT" was created to predict a water's dissolution properties under carbon dioxide treatment.

Program Concept

CO_2 TRT PLOT computes interim (nonequilibrium) pH, CCPP, and Langelier Index (LI) over an incremented range of temperature or carbon dioxide treatment concentrations. The program also computes magnesium hydroxide precipitation potential (MHPP), equilibrium concentrations of alkalinity, Ca^{2+} and Mg^{2+}, and [illegible] of treated or untreated waters. Besides carbon dioxide treatment, the program will predict the outcome of treatment with calcium, magnesium, acid, caustic, lime, soda ash, and bicarbonate.

The basis of the computations is the algorithm of Merrill used in the program "WTR TRTMNT 020583" by Rossum. USACERL modified this program so that a series of input temperatures or dosages, rather than a single value, is fed into the algorithm.

Calculation of LI by the Snoeyink and Jenkins method (LIsn) was added to the original algorithm. This calculation, based on HCO_3^- concentration, produces an index that more closely mimics CCPP at pH values above 9 than that based on total alkalinity (LI).

The program was designed to allow input of pH values measured at temperatures other than 25 °C with no loss of accuracy in computed results. The original program has also been modified to facilitate use of more accurate ionic strength (I) values. Another modification allows the program to read input data from a file.

Program Description

CO_2 TRT PLOT is written in BASIC language to run on IBM-compatible computers. The program is supplied on a single-sided, double-density, 5.25-in. floppy disk formatted by MS-DOS. The program is in the file CTP.BAS. A program that facilitates writing the input data file, WRITE.BAS, is included on the disk. A program listing is also supplied (Appendix A). To allow maximum flexibility in presenting the results, output is to a data file which can be read by the graphics or data base management program of the user's choice.

Merrill's algorithm solves expressions describing equilibria governing systems containing carbonate species, Ca^{2+} and Mg^{2+}.[16] Input concentrations are corrected for ionic strength (I) with the Davies equation. Equilibrium constants are corrected for temperature. Dissolution of $Mg(OH)_2$ is assumed to be very slow, and MHPP is not allowed to be less than 0.

As noted above, flexibility for input of I was added. The modified program allows the user to input a calculated value of I or to have the program calculate I from either (1) conductivity, using the

[16] J. T. Rossum and D. T. Merrill "An Evaluation of the Calcium Carbonate Saturation Indexes," *JAWWA*, Vol 75, No. 2 (1983).

method of Russell[17] or (2) total dissolved solids (TDS) concentration using Langelier's method.[18] The Langelier method is the least accurate. Conductivity is better related to I than is TDS. If the concentrations of all major cations and anions in the water of interest have been determined, calculation with direct input of I is the most accurate method.

Limitations

The program does not account for the formation of ion pairs such as $CaHCO_3^-$, $CaSO_4$, or $CaCO_3$, which may reduce precipitation of $CaCO_3$. It does not describe formation of precipitates other than $CaCO_3$ and $Mg(OH)_2$. Precipitation of $CaSO_4$, $BaSO_4$, SiO_2, $Ca_5(PO_4)_3OH$, and other compounds may occur in some waters.

Alkalinity is assumed to be entirely due to carbonate species. Ions such as $H_3SiO_4^-$ and HPO_4^{2-} contribute to alkalinity in some waters.

The equilibrium constants used are based on expressions describing data obtained between 0 and 50 °C. Use of the program to describe waters at temperatures outside this range may produce inaccurate results.

The model computes the equilibrium states of waters. Kinetic considerations are not included in the computation.

Using CO_2 TRT PLOT

To use the program, load and run the file CTP.BAS in BASIC. The program is menu-driven. All input concentrations are read in milligrams per liter of $CaCO_3$ except that of TDS, which is read only as milligrams per liter. Temperatures are read in Celsius degrees. Output values are in the same units.

Data may be input via the keypad or from the data file CTPin.DAT. To create this file, load and edit the program WRITE.BAS, inserting the appropriate values of alkalinity, Ca^{2+}, Mg^{2+}, and pH. Run this program to create CTPin.DAT.

To obtain an output file containing CCPP, LI, and LIsn values over a range of temperatures, input the initial, final, and incremental temperatures at the "TEMP, CELSIUS (Beg,End,Inc)" prompt. (To obtain values over a decreasing temperature range, input a negative increment.) The program next asks the user to choose an output filename and a title "header" for the file. (Data column headings are included automatically in the output file.)

After the program has run, it will ask if the user desires treatment of the water. The final temperature from the previous computation will be used in this treatment computation. To obtain information related to the equilibrium state of the water at this temperature, choose a treatment and input a dosage of "0". The program will show the equilibrium information, which can be recorded using the "print screen" function of the computer.

To obtain an output file containing CCPP, LI, LIsn, and pH values over a range of carbon dioxide (or other) treatment concentrations, input the temperature at which treatment is desired as both initial

[17] L. L. Russell and D. Jenkins, *Water Chemistry* (John Wiley and Sons, New York, 1980).
[18] J. F. Langelier.

and final temperatures, and "1" as the increment at the "TEMP, CELSIUS (Beg,End,Inc)" prompt. The program will then show the equilibrium state of the water, which again may be recorded by printing the screen. The program next asks for specification of treatment. Input of dosage range and output file attributes are analogous to the procedures for entering temperature ranges.

After results are computed for a treatment, the user may choose to (1) input different starting concentrations ("New Initial Conditions"), (2) enter a new temperature range ("New Temperature"), or (3) exit ("Quit"). If the "New Temperature" option is chosen, the program will disregard the result of the previous treatment. However, if the "New Treatment" option is chosen, the program will use the final temperature of the range last input for treatment temperature.

The two header lines in the output files do not allow these files to be listed by BASIC. However, the files can be listed and printed by the operating system.

Example Runs

The prototype program was used to generate results for three waters taken from different locations. The plots were generated using TECHPLOT, a commercial graphics program.

Case 1 (labeled ISUD) used the following input: alkalinity, 105; Ca^{2+}, 55; Mg^{2+}, 82; pH, 9.5 (at 25 °C). Results were completed for ionic strengths of 0.0039 (calculated for input from the concentrations of Ca^{2+}, Mg^{2+}, and alkalinity) and 0.0082 (computed from the input TDS of 330 mg/L). Carbon dioxide treatment in this and the other cases was set at 25 °C. The computer screens obtained in generating the data for I = 0.0039 are reproduced in Appendix B.

The second case, PM, used the "pipe manifold" water reported by Prakash et al. in Technical Report N-87/16. Input values were: TDS, 120; alkalinity, 110; Ca^{2+}, 40; Mg^{2+}, 45. (Note that the concentrations of the hardness ions have been adjusted to milligrams per liter as $CaCO_3$.)

In the third case, "Fort Ord," water was studied using as input: pH (20 °C), 7.2; alkalinity, 154; TDS, 400; Ca^{2+}, 147; Mg^{2+}, 78.2.

The computer program provided a rapid method of determining dosages required to achieve predetermined pH levels for the various waters tested. Results of the example runs showed that relatively low dosages of carbon dioxide (< 100 mg/L) are adequate to sustain pH values below the calcium carbonate saturation levels. The waters' CCPP values were found to be proportional to the capacity to deposit or dissolve calcium carbonate. The computer model successfully predicted the temperature effect on the scaling potential of the waters tested. This capability can be used to screen various water qualities in terms of scale formation potential in water heating systems.

A copy of the BASIC computer program is available on 5-1/4 in. diskettes for IBM PC and compatible computers. The point of contact for obtaining a copy of the program is Mr. Richard J. Scholze, telephone (217) 373-6743.

4 SUMMARY

This research has produced a model to predict the dissolution properties of potable waters treated with carbon dioxide to remove calcium carbonate scale. The theoretical model was used to write a computer program to make the predictions for a range of temperatures and for treatments other than carbon dioxide.

The literature was surveyed for appropriate models describing the dissolution characteristics of calcium carbonate in water. Two types of models were assessed: those proposing an index to describe the related properties and those describing the dissolution kinetics of calcium. The model best suited to this application (CCPP) was modified to develop a theoretical model for predicting dissolution properties.

The computer program is written in BASIC language for use on IBM and compatible personal computers. The program, called CO_2 TRT PLOT, can predict a water's dissolution characteristics over a range of temperatures and other conditions. It can also make predictions for treatments other than carbon dioxide. The computer program has been tested using waters from three different potable water systems. Results showed that the program can successfully determine dosages required to achieve and sustain predetermined pH levels. The computer model also correctly predicted the effect of temperature on the scaling potential of the various waters tested.

The automated prediction model developed in this study can be used to optimize the design of carbon dioxide treatment regimens for individual distribution systems. A sample of the water to be treated can be subjected to the program to determine the proper dosage based on its propensity for becoming undersaturated, saturated, or oversaturated with respect to carbon dioxide and its capacity for calcium carbonate deposition/dissolution.

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APPENDIX A:

CO_2 TRT PLOT PROGRAM LISTING

```
10 REM "CO2 TRT PLOT" (J.J. Harwood, J.A. Luton), 3/10/88
20 REM adapted from "WTR TRTMNT 020583" (J.R. Rossum),
30 REM which uses Merrill's algorithm.
40 REM The format of the output file for the temperature loop is:
50 REM Temp(Celsius),CCPP,LI,LIsn,pH(interim).
60 REM The format of the output file for the dosage loop is:
70 REM Dosage,CCPP,LI,LIsn,pH(interim).
80 REM Output files are in ASCII, and are " and , delimited for
90 REM use with other programs.
100 REM All concentrations and dosages are in mg/L as CaCO3.
110 REM The paper referenced in the remarks is
120 REM "An evaluation of the calcium carbonate saturation indexes"
130 REM by John R. Rossum and Douglas T. Merrill.
140 REM JAWWA Feb. 1983, 95-100.
150 REM
160 REM**** Arrays
170 REM CCPP(): Calcium Carbonate Precipatation Potential
180 REM S3(): Langlier Index
190 REM SN(): Langlier Index(Snoeyink & Jenkins method)
200 REM H2(): pH at given water temperature(C2)
210 REM
220 REM**** Simple variables
230 REM**  A: alkalinity, equivalent/L
240 REM**  A1: calcium, moles/L
250 REM**  A2: magnesium, moles/L
260 REM**  A3: Mg2+ after ppt of Mg(OH)2
270 REM**  A4: acidity, equivalent/L
280 REM**  A5: alkalinity after ppt of CaCO3
290 REM**  A6: acidity after ppt of Mg(OH)2
300 REM**  A7: alkalinity after ppt of Mg(OH)2
310 REM**  A9: trial value of acidity
320 REM**  B: bicarbonate, moles/L
330 REM**  B1,B2: Value of A in Davies equation at C1,C2
340 REM**  C1: reference temperature(25 Celsius)
350 REM**  C2: temperature(Celsius)
360 REM**  E: mg equivalent weight of CaCO3
370 REM**  E1,E2: Dielectric constant of water at C1,C2
380 REM**  G: carbon dioxide, moles/L
390 REM**  H: hydrogen ion, moles/L
400 REM**  H1: pH at 25 Celsius
410 REM**  H3: pHs
420 REM**  J: carbonate, moles/L
430 REM**  J1,J2: k'1 at C1,C2
440 REM**  K: solubility product of CaCO3
450 REM**  K1: Solubility product of Mg(OH)2 at water temp
460 REM**  KP1,K2: k'2 at C1,C2
470 REM**  L1,L2: k'w at C1,C2
480 REM**  M: mg molecular weight of CaCO3
```

```
490 REM**  M1,M2: -LOG of monovalent activity coefficient at C1,C2
500 REM**  Q: seq (from paper)
510 REM**  Q8: trial value of 2(Ca++) - alky
520 REM**  U: ionic strength, moles/L
530 REM**  X:CaCO3 ppt, moles/L
540 REM**  Z: Mg(OH)2, moles/L
550 KEY OFF
560 CLS
570 LOCATE 9,30
580 PRINT"CO2 TREATMENT PLOTTER
590 LOCATE 12,21
600 PRINT"This program is most accurate with water
610 LOCATE 13,21
620 PRINT"having low SO4, SiO2, and PO4 and with
630 LOCATE 14,21
640 PRINT"temperature 0-50 C.
650 LOCATE 16,21
660 PRINT"All input and output concentrations are
670 LOCATE 17,21
680 PRINT"mg/L CaCO3 except T.D.S. (mg/L).
690 COLOR 0,7
700 LOCATE 23,28:PRINT"Hit SPACEBAR to continue
710 COLOR 7,0
720 A$=INKEY$
730 IF A$<>" " GOTO 720
740 DIM CCPP(550),S3(550),SN(550),H2(550),TREAT$(8)
750 REM This order of variables necessary for enhanced speed
760 H=0
770 Q=0
780 Z=0
790 DD=0
800 A6=0
810 L2=0
820 P=0
830 A2=0
840 A7=0
850 A4=0
860 K2=0
870 R=0
880 Q8=0
890 A3=0
900 J2=0
910 K1=0
920 K=0
930 A=0
940 A1=0
950 A9=0
960 S=0
970 T2=0
980 D=0
990 E=50000!
1000 E=50000!
1010 M=100000!
```

```
1020 M2=0
1030 B2=0
1040 E2=0
1050 U=0
1060 A=0
1070 A1=0
1080 A2=0
1090 H1=0
1100 V$= STRING$(1,34)
1110 W$= STRING$(1,44)
1120 TREAT$(1)="CALCIUM"
1130 TREAT$(2)="MAGNESIUM"
1140 TREAT$(3)="ACID"
1150 TREAT$(4)="CAUSTIC"
1160 TREAT$(5)="LIME"
1170 TREAT$(6)="SODA ASH"
1180 TREAT$(7)="CARBON DIOXIDE"
1190 TREAT$(8)="BICARBONATE"
1200 C1=25
1210 CLS
1220 PRINT"1)  Use data from file 'CTPIN.DAT'
1230 PRINT"2)  Enter all data from keypad
1240 PRINT
1250 INPUT T1
1260 IF T1<1 OR T1>2 THEN 1250
1270 IF T1=2 THEN 1370
1280 OPEN "CTPIN.DAT" FOR INPUT AS #1
1290 LINE INPUT#1,H$
1300 INPUT#1,A,A1,A2,H1
1310 CLOSE#1
1320 PRINT
1330 PRINT"ALKY=";A;" mg/L"
1340 PRINT"CALCIUM=";A1;" mg/L"
1350 PRINT"MAGNESIUM=";A2;" mg/L"
1360 PRINT"pH=";H1
1370 PRINT
1380 PRINT"Select method for ionic strength calculation:
1390 PRINT"  1) Input value
1400 PRINT"  2) Conductivity
1410 PRINT"  3) Total dissolved solids
1420 INPUT T
1430 IF T<1 OR T>3 THEN 1420
1440 ON T GOTO 1450,1490,1540
1450 PRINT"Enter value";
1460 INPUT U
1470 GOTO 1570
1480 REM  L.L. Russell method, PhD thesis, 1976
1490 PRINT"Enter conductivity (micromho)";
1500 INPUT U
1510 U=U/62500!
1520 GOTO 1570
1530 REM  W.F. Langelier method, 1936
1540 PRINT"Enter T.D.S. (mg/L)";
```

```
1550 INPUT U
1560 U=U/40000!
1570 PRINT
1580 IF T1=1 THEN 1710
1590 PRINT"ALKY (AS CACO3)";
1600 INPUT A
1610 PRINT
1620 PRINT"CALCIUM (AS CACO3)";
1630 INPUT A1
1640 PRINT
1650 PRINT"MAGNESIUM (AS CACO3)";
1660 INPUT A2
1670 PRINT
1680 PRINT"pH ";
1690 INPUT H1
1700 PRINT
1710 A=A/E
1720 A1=A1/M
1730 A2=A2/M
1740 PRINT"Temperature of input pH (default is 20 C) ";
1750 INPUT H$
1760 IF H$<>"" THEN 1800
1770 C1=20
1780 PRINT"T=";C1;"C"
1790 GOTO 1810
1800 C1=VAL(H$)
1810 TL=1
1820 PRINT
1830 PRINT"TEMP, CELSIUS (Beg,End,Inc)";
1840 INPUT TB,TE,TI
1850 IF TB<>TE THEN 1880
1860 TI=1
1870 TL=0
1880 L=1/LOG(10)
1890 U1=SQR(U)
1900 T1=C1+273.16
1910 E1=60954!/(C1+389)-68.937
1920 B1=1825000!/(E1*T1)^1.5
1930 M1=B1*((U1/(U1+1))-.2*U)
1940 J1=10^-(3404.71/T1-14.8435+.032786*T1-2*M1)
1950 KP1=10^-(2902.39/T1+.02379*T1-6.498-4*M1)
1960 L1=10^-(4471,33/T1-6,0846+.017053*T1-2*M1
1970 IF TL<>1 THEN 2040
1980 PRINT
1990 PRINT"Enter an output file name";
2000 INPUT F1$
2010 PRINT
2020 PRINT" Enter a header line for the file
2030 INPUT H$
2040 I=0
2050 CLS
2060 LOCATE 11,35
2070 COLOR 23,0
```

```
2080 PRINT"COMPUTING
2090 COLOR 7,0
2100 REM*** Begin temperature loop***
2110 FOR C2=TB TO TE STEP TI
2120 I=I+1
2130 T2=C2+273.16
2140 E2=60954!/(C2+389)-68.937
2150 B2=1825000!/(E2*T2)^1.5
2160 M2=B2*((U1/(U1+1))-.2*U)
2170 J2=10^-(3404.71/T2-14.8435+.032786*T2-2*M2)
2180 K2=10^-(2902.39/T2+.02379*T2-6.498-4*M2)
2190 L2=10^-(4471.33/T2-6.0846+.017053*T2-2*M2)
2200 K1=10^-(.0175*C2+9.97-6*M2)
2210 K=10^(13.87-3059/T2-.04035*T2+8*M2)
2220 H=10^(M1-H1)
2230 Q=H-L1/H
2240 P=(1+2*H/J1)/(1+2*KP1/H)
2250 A4=A*P+P*Q+Q
2260 IF L1/H<=A+H GOTO 2340
2270 PRINT
2280 PRINT"There is an error in your data at";C2;"Celsius
2290 PRINT"Alky must be greater than hydroxyl
2300 PRINT"Please reenter initial conditions
2310 PRINT
2320 PRINT
2330 GOTO 1270
2340 IF C1=C2 THEN 2460
2350 H=.001
2360 DD=10
2370 H=H/(DD+1)
2380 Q=H-L2/H
2390 P=(1+2*H/J2)/(1+2*K2/H)
2400 A9=(A+Q)*P+Q
2410 IF A4<A9 THEN 2370
2420 H=H*(DD+1)
2430 DD=DD/2
2440 IF DD<.0001 THEN 2460
2450 GOTO 2370
2460 H2(I)=M2-L*LOG(H)
2470 R=2+H/K2
2480 B=(A+Q)/(1+2*K2/H)
2490 G=H*B/J2
2500 J=(A+Q)/R
2510 IF TL=0 THEN GOSUB 4700
2520 IF A1=0 THEN 2570
2530 F=1-K2*A1/K
2540 B=K2*(2-A1*A/K)
2550 C=K2*L2*A1/K
2560 IF B^2>4*F*C THEN 2630
2570 IF TL=0 THEN 2600
2580 PRINT"LANGELIER INDEX HAS NO REAL VALUE AT"C2"CELCIUS
2590 GOTO 2610
2600 PRINT"LANGELIER INDEX HAS NO REAL VALUE
```

```
2610 S=-1
2620 GOTO 2670
2630 H3=(SQR(B^2-4*F*C)-B)/2/F
2640 S3(I)=H2(I)-M2+L*LOG(H3)
2650 IF TL=0 THEN PRINT USING"LANGELIER INDEX            ##.##";S3(I)
2660 S=SGN(S3(I))
2670 HN=A1*(A-L2/H+H)*(K2/K)*(H/(2*K2+H))
2680 SN(I)=H2(I)-M2+L*LOG(HN)
2690 IF TL=0 THEN PRINT USING"LANGELIER INDEX SN         ##.##";SN(I)
2700 REM Find correct CCPP root by halving method
2710 DD=S/2
2720 H=H/(1-DD)
2730 Z=A2-K1*H*H/L2/L2
2740 IF Z<0 THEN Z=0
2750 A3=A2-Z
2760 A7=A-2*Z
2770 A6=A4+2*Z
2780 P=(1+2*H/J2)/(1+2*K2/H)
2790 Q=H-L2/H
2800 R=2+H/K2
2810 Q8=2*K*R*P/(A6-Q)-(A6-Q)/P+Q-2*A1+A7
2820 IF ABS(DD)<.000001 THEN 2880
2830 IF A6-Q<0 THEN 2850
2840 IF S*Q8<0 THEN 2720
2850 H=H*(1-DD)
2860 DD=DD/2
2870 GOTO 2720
2880 A5=(A6-Q)/P-Q
2890 X=(A7-A5)/2
2900 A2=A3
2910 A=A7
2920 CCPP(I)=X*M
2930 NEXT
2940 C2=C2-TI
2950 IF TL=0 THEN 3070
2960 OPEN F1$ FOR OUTPUT AS #1
2970 PRINT#1,H$
2980 PRINT#1,"T LOOP
2990PRINT#1,V$"Temp"V$W$V$"CCPP"V$W$V$"LI"V$W$V$"LISN"V$W$V$"PH(INTERIM)"V$W$
3000 I=0
3010 FOR T=TB TO TE STEP TI
3020 I=I+1
3030 PRINT#1,USING"###.##,";T,CCPP(I),S3(I),SN(I),H2(I)
3040 NEXT
3050 CLOSE#1
3060 GOTO 3080
3070 GOSUB 4820
3080 CLS
3090 PRINT"SELECT TREATMENT at";C2;"Celsius"
3100 PRINT"  1. CALCIUM          5. LIME"
3110 PRINT"  2. MAGNESIUM        6. SODA ASH"
3120 PRINT"  3. ACID             7. CARBON DIOXIDE"
3130 PRINT"  4. CAUSTIC          8. BICARBONATE"
```

```
3140 PRINT TAB(10)"0. TERMINATES SELECTIONS"
3150 INPUT T
3160 IF T=0 THEN 5020
3170 IF T<0 OR T>8 THEN 3150
3180 DL=1
3190 PRINT TREAT$(T);" DOSE(Beg,End,Inc) ";
3200 INPUT DB,DE,DI
3210 IF DB<>DE THEN 3250
3220 DL=0
3230 DI=1
3240 GOTO 3310
3250 PRINT
3260 PRINT"  Enter an output file name";
3270 INPUT F2$
3280 PRINT
3290 PRINT"  Enter a header line for the file
3300 INPUT H$
3310 I=0
3320 CLS
3330 LOCATE 11,35
3340 COLOR 23,0
3350 PRINT"COMPUTING
3360 COLOR 7,0
3370 REM*** Dosage loop  ***
3380 FOR D=DB TO DE STEP DI
3390 I=I+1
3400 REM This is necessary to preserve interim alky for loop calculations
3410 ADUM=A
3420 ON T GOSUB 3580,3630,3680,3750,3820,3910,3970,4030
3430 NEXT
3440 IF DL=0 GOTO 5070
3450 OPEN F2$ FOR OUTPUT AS #1
3460 PRINT#1,H$
3470 PRINT#1,"D LOOP
3480PRINT#1,V$"DOSE"V$W$V$"CCPP"V$W$V$"LI"V$W$V$"LISN"V$W$V$"PH(INTERIM"V$W$
3490 I=0
3500 FOR D=DB TO DE STEP DI
3510 I=I+1
3520 PRINT#1,USING"###.##,";D,CCPP(I),S3(I),SN(I),H2(I)
3530 NEXT
3540 CLOSE#1
3550 GOTO 5020
3560 REM Adjust concentrations for dosage loop
3570 REM Calcium
3580 A1=A1+D/M
3590 GOSUB 4110
3600 A1=A1-D/M
3610 RETURN
3620 REM Magnesium
3630 A2=A2+D/M
3640 GOSUB 4110
3650 A2=A2-D/M
3660 RETURN
```

```
3670 REM Acid
3680 A=A-D/E
3690 A4=A4+D/E
3700 GOSUB 4110
3710 A=ADUM
3720 A4=A4-D/E
3730 RETURN
3740 REM Caustic
3750 A=A+D/E
3760 A4=A4-D/E
3770 GOSUB 4110
3780 A=ADUM
3790 A4=A4+D/E
3800 RETURN
3810 REM Lime
3820 A1=A1+D/M
3830 A=A+D/E
3840 A4=A4-D/E
3850 GOSUB 4110
3860 A1=A1-D/M
3870 A=ADUM
3880 A4=A4+D/E
3890 RETURN
3900 REM Soda Ash
3910 A=A+D/E
3920 GOSUB 4110
3930 A=ADUM
3940 RETURN
3950 REM Carbon Dioxide
3960 A=A-D/E
3970 A4=A4+D/E
3980 GOSUB 4110
3990 A=ADUM
4000 A4=A4-D/E
4010 RETURN
4020 REM Bicarbonate
4030 A=A+D/E
4040 A4=A4+D/E
4050 GOSUB 4110
4060 A=ADUM
4070 A4=A4-D/E
4080 RETURN
4090 REM*** These calculations same as for temp loop ***
4100 REM (separated to minimize branching)
4110 H=.001
4120 DD=10
4130 H=H/(DD+1)
4140 Q=H-L2/H
4150 P=(1+2*H/J2)/(1+2*K2/H)
4160 A9=(A+Q)*P+Q
4170 IF A4<A9 THEN 4130
4180 H=H*(DD+1)
4190 DD=DD/2
```

```
4200 IF DD<.0001 THEN 4220
4210 GOTO 4130
4220 H2(I)=M2-L*LOG(H)
4230 R=2+H/K2
4240 B=(A+Q)/(1+2*K2/H)
4250 G=H*B/J2
4260 J=(A+Q)/R
4270 IF DL=0 THEN GOSUB 4700
4280 IF A1=0 THEN 4330
4290 F=1-K2*A1/K
4300 B=K2*(2-A1*A/K)
4310 C=K2*L2*A1/K
4320 IF B^2>4*F*C THEN 4390
4330 IF DL=0 THEN 4360
4340 PRINT"LANGELIER INDEX HAS NO REAL VALUE AT DOSAGE"D
4350 GOTO 4370
4360 PRINT"LANGELIER INDEX HAS NO REAL VALUE
4370 S=-1
4380 GOTO 4430
4390 H3=(SQR(B^2-4*F*C)-B)/2/F
4400 S3(I)=H2(I)-M2+L*LOG(H3)
4410 IF DL=0 THEN PRINT USING"LANGELIER INDEX          ##.##";S3(I)
4420 S=SGN(S3(I))
4430 HN=A1*(A-L2/H+H)*(K2/K)*(H/(2*K2+H))
4440 SN(I)=H2(I)-M2+L*LOG(HN)
4450 IF DL=0 THEN PRINT USING"LANGELIER INDEX SN       ##.##";SN(I)
4460 DD=S/2
4470 H=H/(1-DD)
4480 Z=A2-K1*H*H/L2/L2
4490 IF Z<0 THEN Z=0
4500 A3=A2-Z
4510 A7=A-2*Z
4520 A6=A4+2*Z
4530 P=(1+2*H/J2)/(1+2*K2/H)
4540 Q=H-L2/H
4550 R=2+H/K2
4560 Q8=2*K*R*P/(A6-Q)-(A6-Q)/P+Q-2*A1+A7
4570 IF ABS(DD)<.000001 THEN 4630
4580 IF A6-Q<0 THEN 4600
4590 IF S*Q8<0 THEN 4470
4600 H=H*(1-DD)
4610 DD=DD/2
4620 GOTO 4470
4630 A5=(A6-Q)/P-Q
4640 X=(A7-A5)/2
4650 A2=A3
4660 A=A7
4670 CCPP(I)=X*M
4680 IF DL=0 THEN GOSUB 4820
4690 RETURN
4700 CLS
4710 PRINT"INTERIM STATE:"
4720 PRINT"ANALYSIS AT"C2"CELCIUS
```

```
4730 PRINT USING"CALCIUM                    ###.##";A1*M
4740 PRINT USING"MAGNESIUM                   ###.##";A2*M
4750 PRINT USING"PH                        ##.##";H2(I)
4760 PRINT USING"ALKALINITY                 ###.##";A*E
4770 PRINT USING"  CARBON DIOXIDE            ###.##";M*G
4780 PRINT USING"  BICARBONATE              ###.##";E*B
4790 PRINT USING"  CARBONATE                ###.##";M*J
4800 PRINT USING"ACIDITY                   ###.##";A4*E
4810 RETURN
4820 PRINT
4830 PRINT"EQULIBRATED STATE:"
4840 PRINT USING"PH                        ##.##";M2-L*LOG(H)
4850 PRINT USING"CALCIUM                    ###.##";M*(A1-X)
4860 PRINT USING"MAGNESIUM                   ###.##";M*A3
4870 PRINT USING"ALKALINITY                 ###.##";E*(A7-2*X)
4880 PRINT"PRECIPITATION POTENTIALS"
4890 PRINT USING"    CACO3                 ####.##";CCPP(I)
4900 PRINT USING"    MG(OH)2               ####.##";Z*M
4910 PRINT
4920 PRINT
4930 COLOR 0,7
4940 LOCATE 23,30
4950 PRINT" Hit SPACEBAR to continue ";
4960 COLOR 7,0
4970 PRINT
4980 A$=INKEY$
4990 IF A$<>" " GOTO 4980
5000 CLS
5010 RETURN
5020 LOCATE 11,35
5030 PRINT"          "
5040 PRINT
5050 PRINT
5060 PRINT
5070 PRINT"1)  New initial conditions"
5080 PRINT"2)  New temperature"
5090 PRINT"3)  New treatment"
5100 PRINT"0)  Quit"
5110 INPUT T
5120 IF T<0 OR T>3 THEN 5110
5130 CLS
5140 ON T GOTO 1220,1810,3080,5160
5150 PRINT
5160 PRINT"Run PLOT.BAS to screen plot the data in the output file(s)
5170 PRINT
5180 KEY ON
5190 END
```

APPENDIX B:

COMPUTER SCREENS DURING TEMPERATURE AND TREATMENT RANGE RUNS

CO_2 TREATMENT PLOTTER

This program is most accurate with water having low SO_4, SiO_4, and PO_4 and with temperature 0 TO 50 °C.

All input concentrations are mg/L $CaCO_3$ except TDS (mg/L).

Hit SPACEBAR to continue

1) Use data from file 'CTPin.DAT'
2) Enter all data from keypad

? 1

ALKY= 105 mg/L
CALCIUM= 55 mg/L
MAGNESIUM= 82 mg/L
pH= 9.5

Select method for ionic strength calculation:
  1) Input value
  2) Conductivity
  3) Total dissolved solids
? 1
Enter value? .0039

Temperature of input pH (default is 20 C) ? 25

TEMP, CELSIUS (Beg,End,Inc)? 0,50,5

  Enter an output file name? ISUD1.DAT

  Enter a header line for the file
? ISUD 1
SELECT TREATMENT at 50 Celsius

1. CALCIUM	5. LIME
2. MAGNESIUM	6. SODA ASH
3. ACID	7. CARBON DIOXIDE
4. CAUSTIC	8. BICARBONATE
	0. TERMINATES SELECTIONS

? 0
1) New initial conditions

2) New temperature
3) Quit
? 2

TEMP, CELSIUS (Beg,End,Inc)? 25,25,O
INTERIM STATE:
ANALYSIS AT 25 CELSIUS

CALCIUM	55
MAGNESIUM	82
PH	9.5
ALKALINITY	105
CARBON DIOXIDE	.1
BICARBONATE	75.76
CARBONATE	27.54
ACIDITY	74.15
LANGELIER INDEX	1.5
LANGELIER INDEX SN	1.36

EQUILIBRATED STATE:

PH	8.479999
CALCIUM	25.97
MAGNESIUM	82
ALKALINITY	75.97
PRECIPITATION POTENTIALS	
$CaCo_3$	29.03
$Mg(OH)_2$	0

Hit SPACEBAR to continue
SELECT TREATMENT at 25 Celsius

1. CALCIUM	5. LIME
2. MAGNESIUM	6. SODA ASH
3. ACID	7. CARBON DIOXIDE
4 CAUSTIC	8. BICARBONATE

0. TERMINATES SELECTIONS

? 7
CARBON DIOXIDE DOSE(Beg,End,Inc) ? 0,150,15

Enter an output file name? ISUD.DAT

Enter a header line for the file
? ISUD 2
1) New initial conditions
2) New temperature
3) New treatment
0) Quit
? 0
0

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